Thermal Diffusivity of 4-inch Diamond Wafers Deposited with Multi-Cathode dc-Plasma Assisted CVD [1]

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[1] Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A

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ABSTRACT

Thermal diffusivity map of diamond wafers with 4 inches diameter was obtained by a converging thermal wave technique in a nondestructive and non-contact way. Diamond wafers were deposited by the seven-cathode dc-plasma assisted chemical vapor deposition in the feeding gases of varying CH_4 concentration (6 – 10 % in volume) in pure hydrogen and also varying the power of the plasma. Six cathodes were located at the apexes of a hexagon with an arm distance 4.3 cm with a central cathode. The wafer deposited at low power plasma (13.47 kW) is shown three circular zones on the thermal diffusivity map. The thermal diffusivity shows the lowest value at the center. It increases up to about 10 % in the radius of 2 - 3 cm, and then decreases with further increases of the radius. The optical photograph and the Raman lines of the wafer show similar patterns with that of the thermal diffusivity. These are affected by the locations of the cathodes in the deposition chamber when the plasma power is low. Diamond wafer deposited at high power plasma (20.58 kW) with high concentration of methane (10 % in volume) is shown higher values of thermal diffusivity and better uniformity than the wafer deposited at low power and low methane concentration. A fine crack can be located on a wafer by the converging thermal wave technique.

KEY WORDS : converging thermal wave technique; CVD diamond; diamond wafer; thermal diffusivity;

1. INTRODUCTION

Diamond has good physical properties such as high thermal conductivity, high electrical resistivity, low thermal expansion coefficient, and good mechanical property. Chemical vapor deposition (CVD) diamond growth has reached maturity and availability. The synthetic diamond wafer can be used for a thermal management substrate of high power electronic packages. Large area diamond wafers are required for this application. Recently, it was reported that the diamond wafers with large area could be deposited by DC arc-jet method [1] and DC PACVD (direct current plasma assisted vapor deposition) method [2,3]. The evaluation of the quality for the large area diamond is an important issue. Thermal diffusivity is one of good physical properties to characterize the diamond wafer.

Thermal property is a difficult physical property to measure accurately. In case of diamond, it is more difficult because CVD diamond has high thermal conductivity and has a rough surface. The steady state heated bar technique was proved to be the most accurate method in the second round robin measurement [4]. However, this method requires a long preparation time and a well-defined sample geometry. The laser flash method is sensitive to the sample thickness.

A Converging thermal wave technique to measure the in-plane thermal diffusivity is independent of specimen shape and size [5,6]. Annular ring of pulsed laser beam is irradiated on a specimen as a heating source and the temperature variation at the center of the ring is measured with an IR-detector. This method is non-contacting and nondestructive.

We measured thermal diffusivity of free standing 4-inch diameter diamond wafers with converging thermal wave technique at room temperature. In order to verify the accuracy of the converging thermal wave technique, we measured thermal diffusivity of high purity copper and aluminum. The diamond wafers were deposited with multi-cathode direct current plasma assisted chemical vapor deposition [2,3].

2. MEASUREMENTS

2.1 Experimental apparatus

A converging thermal wave technique was used to measure the in-plane thermal diffusivity of 4-inch diamond wafers without breaking. The schematic diagram of the experimental apparatus is shown Fig. 1. Pulsed Nd:Yag laser with energy of 0.9 J/pulse, wavelength of 1.06 μm, diameter of 1 cm, and pulse duration time of 0.3 msec is used for a heating source. The pulse duration time is short enough to compare with the characteristic thermal diffusion time. If the pulse duration time is too short, laser pulse ablates the materials on the surface of sample instead of thermal heating. In order to produce annular laser beam as heating source, laser beam is passed through a convex lens and an axicon (lens of conical cross section) that has an apex angle of 5 °. The focal length of the convex lens is 12.5 cm. The diameter of the annular ring is 13 mm and the width is a few tens of micrometers. The diameter is measured by a cathetometer within ±10 μm. The diameter can be controlled by a focal length of convex lens, an apex angle of axicon and a distance between lens and axicon. The annular laser beam is focused on the front surface of a diamond wafer. Temperature variation at the center of the heating ring on the back surface is measured with a HgCdTe (Mercury Cadmium Telluride) detector that is cooled with liquid nitrogen. An aperture with diameter of 1mm is located in front of an IR-detector. The output signal from the IR-detector is measured with a 500 MHz digital oscilloscope through an pre-amplifier.

2.2 Data Analyzing Methods

The detail analysis of a thermal converging wave method is presented at the other part of this symposium by Joo et al. [7]. Brief description about the data analyzing method is given as following. For a thin sample, the temperature variation at the center of the heating ring is given by [5]

$$T(t) = \frac{KR^2}{at}\exp\left(-\frac{R^2}{4at}\right) \qquad (1)$$

where K is a multiplicative constant with function of E, ρ, and c. E is the energy absorbed per unit thickness, ρ is the density and c is the specific heat. α is the in-plane thermal diffisivity. R is the radius of the heating ring. The time to reach the maximum temperature at the center of the heating ring can be obtained by differentiating the above equation. The in-plane thermal diffisivity is given by

$$a = \frac{R^2}{4t_m} \qquad (2)$$

where t_m is the time when temperature is the maximum. A computer program with the nonlinear least squares method is used to find the t_m on the trace of temperatre variation as function of time. The fitting curve and the trace of temperature variation are shown in Fig. 2. From the fitting curve, the t_m can be given within $\pm$ 0.2 msec.

2.3 Specimen Preparations

The diamond wafers were deposited by the multi cathodes (seven) direct current plasma assisted chemical vapor deposition [2,3]. The schematic diagram of the dc-plasma assisted chemical vapor deposition is shown in Fig. 3. The six cathodes are arranged at the apexes of a hexagon with an arm distance of 4.3 cm and one cathode is located at the center. Each cathode is connected with a dc power supply independently. The distance between the cathodes and the substrate is 4 cm. This array of the cathodes are designed to enlarge the deposition area with a good plasma distribution. The substrate is rotated during deposition throughout the whole process. The feeding gas is varied with a CH_4 concentration in pure hydrogen. The gas flow rate is 100 sccm (standard cubic centimeter per minute) and the pressure in the chamber is maintained 100 torr. After deposition, the diamond wafer is self-extracted from the substrate by the difference of thermal expansion coefficient between the film and substrate when the substrate is cooled.

Two diamond wafers were deposited with varying the CH_4 concentration and the applied power for plasma. The diamond wafer with CH_4 concentration of 6 % was deposited with 1.9 kW for each cathode. Thus, the total power was 13.4 kW. The average deposition rate was 5 $\mu m \cdot hr^{-1}$ throughout the deposition process. A pyrometer was used to monitor the substrate temperature. The average substrate temperature was 1250 °C. The thickness distribution on the wafer is 850-1000 μm. The diamond wafer with CH_4 concentration of 10 % was deposited with the total power of 20.58 kW. The deposition rate was 9.4-9.6 μm/hr and the thickness was 800-876 μm. The deposition temperature was 1276 °C. This wafer has a crack. Dried graphite fluid was sprayed uniformly on both surface of diamond wafer with a few micrometer thickness. This graphite coated layer not only helps for a uniform absorption of the incoming pulse but also gives a uniform emissivity to the IR-detector.

3. RESULTS

High purity copper and aluminum foils with various thickness were used to measure thermal diffusivity with converging thermal wave technique in order to investigate the thickness effect. In our calculation, thermal diffusivity of diamond is decreased when the thickness is larger than 2.5 mm [7]. The thermal diffusivities of high purity copper with thickness of 50, 100, 300, and 500 μm are 1.163 ± 0.023 $cm^2 \cdot sec^{-1}$. These values agree with the literature value of 1.1234 $cm^2 \cdot sec^{-1}$ within 4 %. The thermal diffusivities of aluminum foils with thickness of 50 and 100 μm are 0.916 ± 0.018 $cm^2 \cdot sec^{-1}$. The literature value for aluminum is 0.8418 $cm^2 \cdot sec^{-1}$ and they agree within 8.8 % [8].

The specimen size effect was studied by Joo et al. [7]. When the sample size is smaller than twice the diameter of the heating ring, the t_m increases rapidly with a broader peak and the temperature decreases very slowly after the maximum. The results were confirmed in the experiment with copper. In this reason, the region inside 1cm from the edge of the wafer was excluded from the measurements. At the same reason, thermal diffusivity near a crack in the diamond wafer is shown smaller than the thermal diffusivity measured far from crack.

Thermal diffusivity distribution on the diamond wafer with CH_4 concentration of 6 % is shown in Fig. 4 as a contour map of the octagonal colored area. The measured points were 175 on this wafer at an interval distance of 5 mm in X and Y direction. The dark colored region in the contour map represents higher thermal diffusivity than the whiter region. It is shown three different diffusivity regions. The minimum thermal diffusivity is measured 6.4 $cm^2 \cdot sec^{-1}$ near the center of the wafer. The maximum thermal diffusivity is measured 7.2 $cm^2 \cdot sec^{-1}$. The highest thermal diffusivity region is located between 1 cm and 3 cm from center of the wafer. Thermal diffusivity is shown the intermediate values outside of the radius 3 cm from the center of the wafer. These regions are shown a symmetric ring pattern. Raman peaks showed the similar trends [3]. The FWHM (Full With Half Maximum) of the Raman peak at 2 cm from the center is 4.0 cm^{-1} and the peak shape is the sharpest. The Raman lines at the other places are shown higher values of the FWHM. The FWHM is 4.5 cm^{-1} at the center and 5.0 cm^{-1} at the place of 4 cm from the center of the diamond wafer.

An optical photograph of the wafer is shown in Fig. 5. A similar pattern can be seen like the thermal diffusivity contour map. The black colored ring is the same area of the highest thermal diffusivity region in the contour. The white central and the outer ring correspond to the lowest and the intermediate thermal diffusivity contour. The translucent region is directly underneath the cathodes. The highest thermal diffusivity region is located between the central cathode and the outer cathodes

Thermal diffusivity distribution on the diamond wafer with 10 % CH_4 concentration is shown in Fig. 6 as a contour map. The measured points are 37 on this specimen. This wafer has a crack. Thermal diffusivity is shown slightly higher than the diamond wafer of 6 % CH_4. Thermal diffusivity distribution is 5.0-7.6 $cm^2 \cdot sec^{-1}$ and does not have ring patterns like the diamond wafer of 6 % CH_4 concentration. The increment of thermal diffusivity might be the reason of the higher plasma power. Diamond wafer of better quality could be obtained by increasing the power of the plasma with higher concentration of CH_4 with multi-cathode dc-PACVD.

Thermal diffusivities are shown relatively low values around the region of a crack. It was not easy to locate the fine crack by visual inspection right after the deposition. The crack location can be seen clearly on the diffusivity contour map.

4. CONCLUSION

Thermal diffusivity of 4-inch diamond wafers has been measured by the converging thermal wave technique. The diamond wafers have been synthesized by 7-cathode dc-PACVD. Thermal diffusivity distribution on the diamond wafers is given as a contour map. Three circular concentric thermal diffusivity patterns can be found in 6 % CH_4 diamond wafer. These patterns are related with the locations of the seven cathodes. Thermal diffusivity of 10 % CH_4 diamond wafer is shown higher than that of 6 % CH_4 diamond wafer deposited with smaller power of plasma. Higher power and CH_4 concentration improves the uniform distribution of thermal diffusivity on the diamond wafer with faster growth rate. The location of a fine crack hardly seen visually on the diamond wafer could be detected by the converging thermal wave technique.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Information and Communication.

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FIGURE CAPTIONS

Fig. 1. The schematic diagram of the apparatus for the converging thermal wave technique.

Fig. 2. The trace of temperatre variation detected at the center of diamond wafer. The line is the fitting curve.

Fig. 3. The schematic diagram of the seven-cathode DC PACVD.

Fig. 4. Thermal diffusivity distribution on 6 % CH_4 diamond wafer.

Fig. 5. A photograph of 6 % CH_4 diamond wafer.

Fig. 6. Thermal diffusivity distribution on 10 % CH_4 diamond wafer.

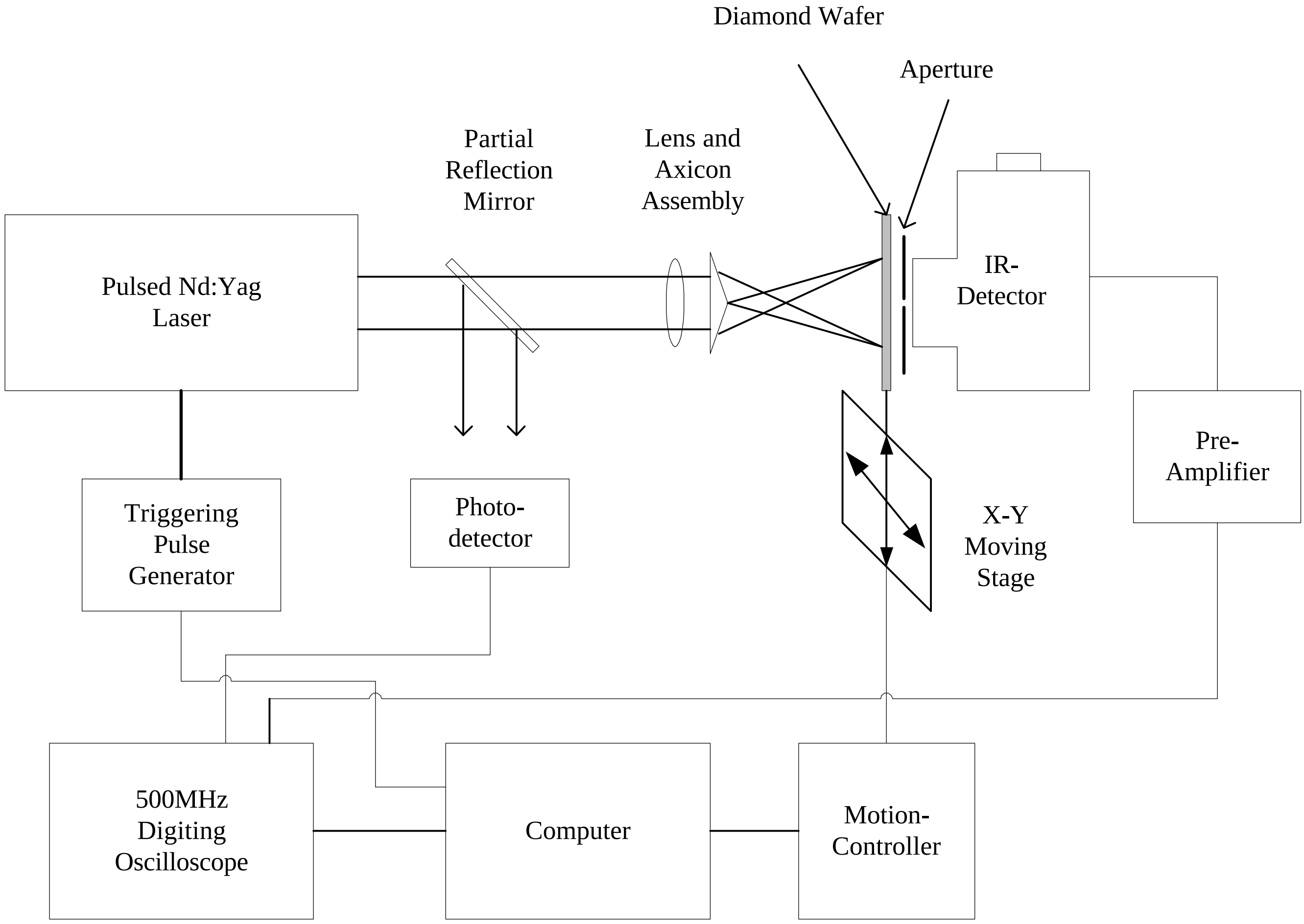
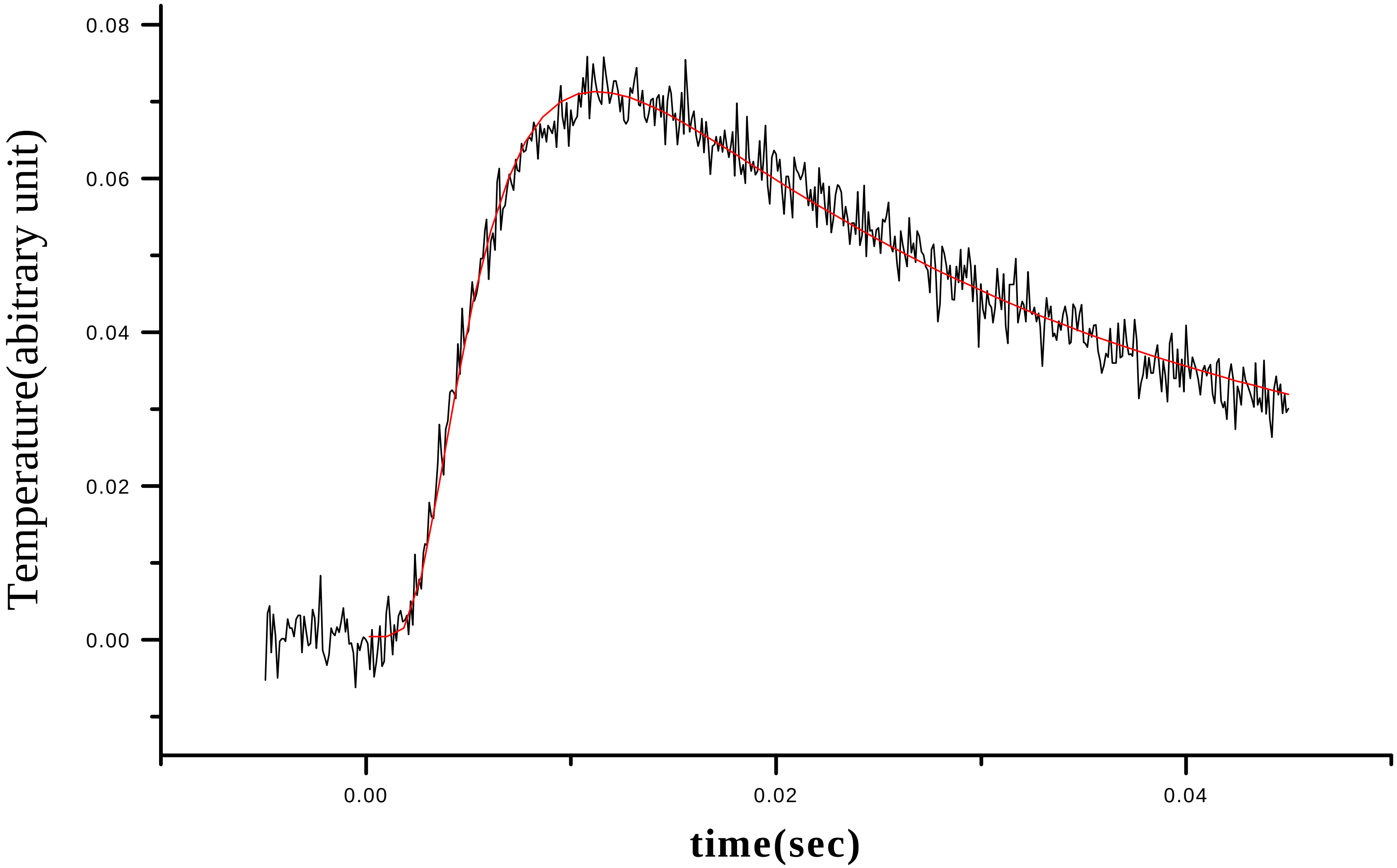

Diamond Wafer
Aperture
Partial Reflection Mirror
Lens and Axicon Assembly
Pulsed Nd:Yag Laser
IR-Detector
Pre-Amplifier
Triggering Pulse Generator
Photo-detector
X-Y Moving Stage
500MHz Digiting Oscilloscope
Computer
Motion-Controller

Fig. 1



0.08
0.06
0.04
0.02
0.00
Temperature(abitrary unit)
0.00
0.02
0.04
time(sec)

Fig. 2

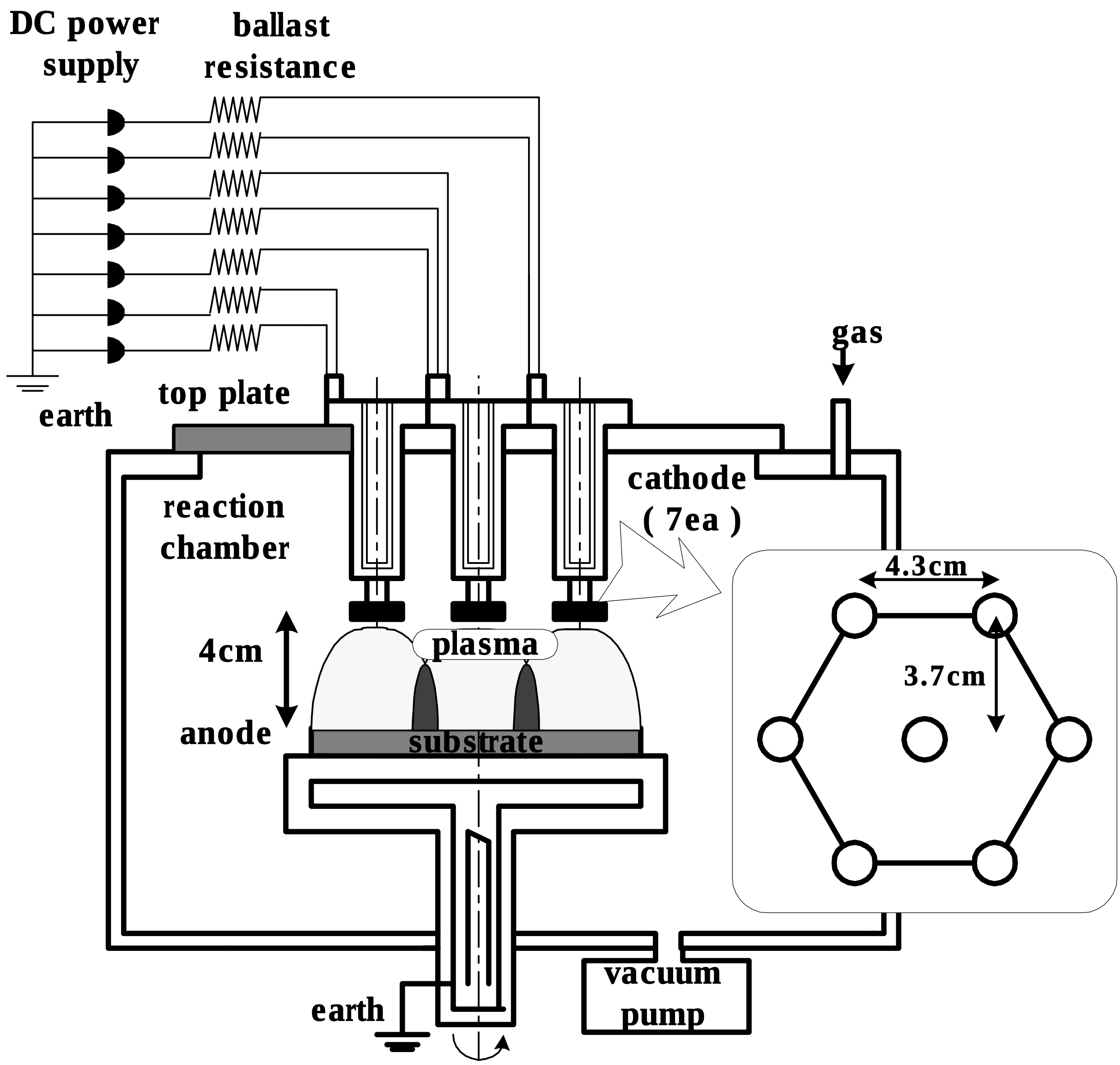

DC power supply
ballast resistance
earth
top plate
gas
cathode (7ea)
reaction chamber
4.3cm
3.7cm
4cm
plasma
anode
substrate
earth
vacuum pump

Fig. 3

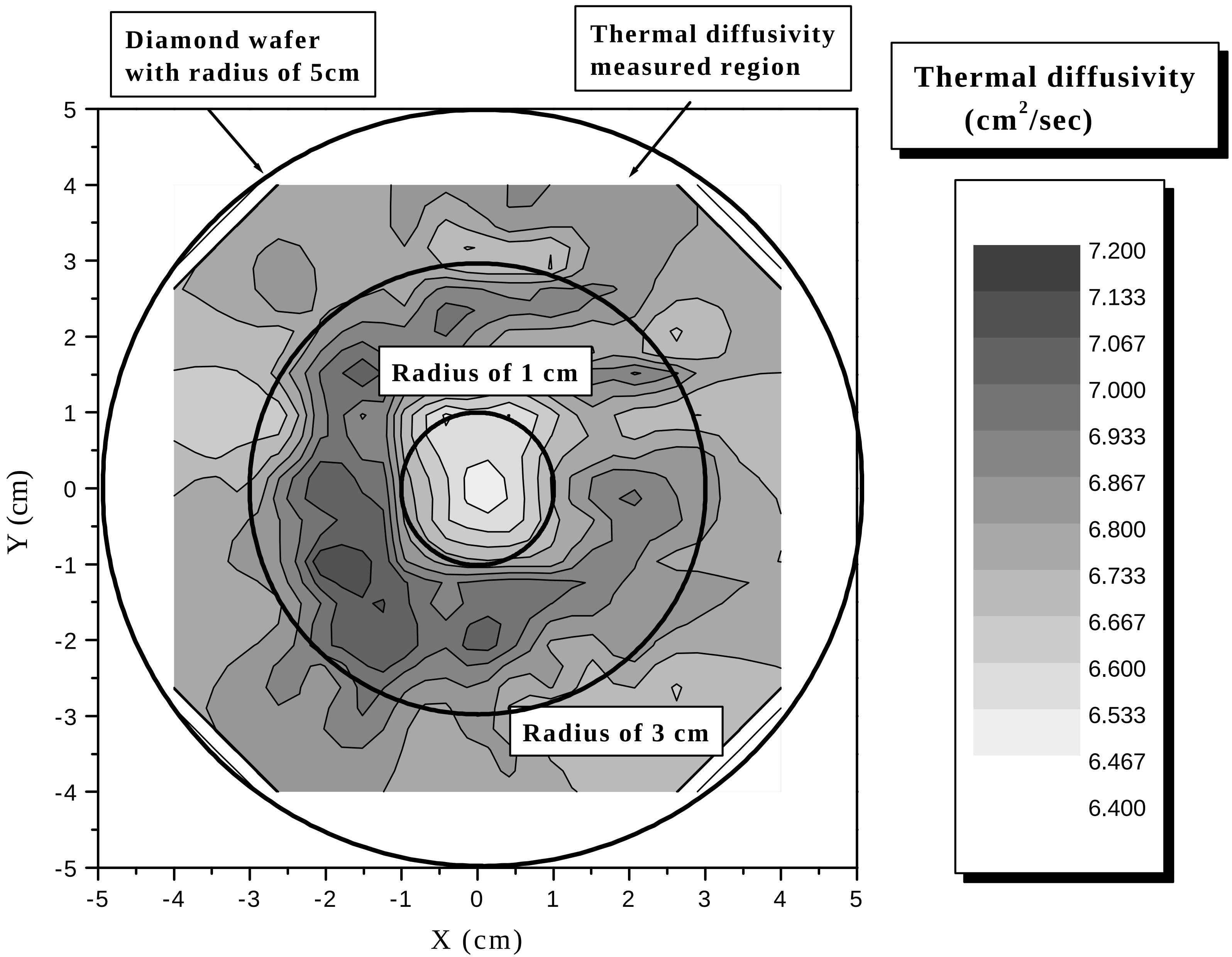
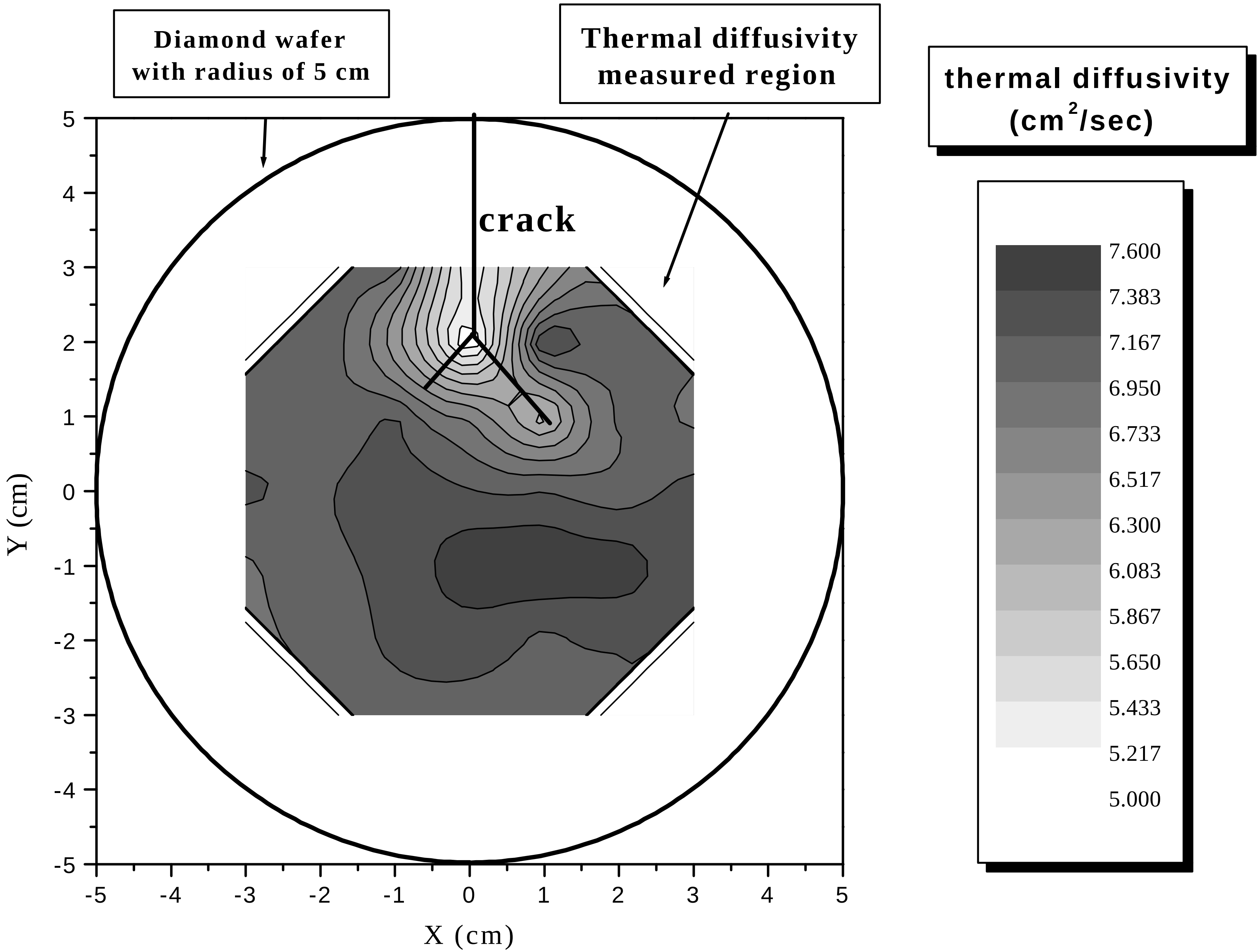

Diamond wafer
with radius of 5cm
Thermal diffusivity
measured region
Thermal diffusivity
(cm^2/sec)
Radius of 1 cm
Radius of 3 cm
7.200
7.133
7.067
7.000
6.933
6.867
6.800
6.733
6.667
6.600
6.533
6.467
6.400
Y (cm)
X (cm)
5
4
3
2
1
0
-1
-2
-3
-4
-5

Fig. 4

Fig. 5



Diamond wafer
with radius of 5 cm
Thermal diffusivity
measured region
thermal diffusivity
(cm²/sec)
crack
7.600
7.383
7.167
6.950
6.733
6.517
6.300
6.083
5.867
5.650
5.433
5.217
5.000
Y (cm)
X (cm)
5
4
3
2
1
0
-1
-2
-3
-4
-5

Fig. 6